Theory of high-symmetry tetramer single molecule magnets

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We present a microscopic theory of single molecule magnets. From our exact single-ion spin matrix elements for four arbitrary spins, we study the single-ion anisotropy of equal spins exhibiting T_d, D_{2d}, or C_{4v} molecular group symmetry. Each group generates site-dependent single-ion anisotropy. For weak anisotropy, accurate Hartree expressions for the magnetization, specific heat, electron paramagnetic resonance (EPR) absorption and inelastic neutron scattering cross-section are given. For D_{2d}, azimuthal single-ion anisotropy leads to the observed Ni_4 EPR splittings.

Single molecule magnets (SMM's) have been a topic of great interest for more than a decade,[1] because of their potential uses in quantum computing and/or magnetic storage,[2] which are possible due to magnetic quantum tunneling (MQT) and entangled states. In fits to a wealth of data, the Hamiltonian within an SMM was assumed to be the Heisenberg exchange interaction plus weaker global (total, or giant) spin anisotropy interactions, with a fixed overall global spin quantum number s.[1] MQT and entanglement were studied in this simple model.

The simplest SMM's are dimers.[3, 4] Surprisingly, two antiferromagnetic dimers, an Fe_2 and a Ni_2, appear to have substantial single-ion anisotropy without any appreciable global anisotropy.[4, 5, 6] Although the most common SMM's have ferromagnetic (FM) intramolecular interactions and contain $n \geq 8$ magnetic ions,[7] a number of intermediate-sized FM SMM's with $n = 4$ and rather simple molecular structures were recently studied. Co_4 and Cr_4 have $s = 6$ ground states with spin 3/2 ions on the corners of tetrahedrons.[8, 9] A number of high symmetry $s = 4$ ground state Ni_4 structures with spin 1 ions were reported.[10, 11, 12] Inelastic neutron scattering (INS) experiments provided strong evidence for single-ion anisotropy in Co_4 and a Ni_4.[9, 10] Fits to electron paramagnetic resonance (EPR) Ni_4 data assuming a fixed s were also problematic.[13]

Yet there is no microscopic model of FM SMM's in which the MQT and entanglement issues crucial for quantum computing can be understood. To analyze the differences between single-ion and global anisotropy in FM systems, we found exact expressions for the single-ion spin matrix elements of four general spins, and compared global and single-ion anisotropies in the Hartree approximation for the magnetization, specific heat, EPR and INS transitions for equal-spin SMM tetramers with molecular group T_d, D_{2d}, and C_{4v} symmetries. Surprisingly, we also found that each molecular group symmetry generates site-dependent single-ion anisotropy, and that azimuthal D_{2d} single-ion anisotropy has a continuous symmetry, observed as splittings in the Ni_4 EPR resonances.[11]

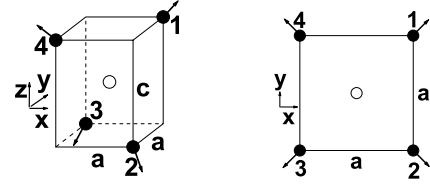We assume four equal spins s_1 sit on opposite corners of

FIG. 1: D_{2d} (left) and C_{4v} (right) ion sites (filled). Circle: origin. Arrows: local axial (left), azimuthal (right) vectors.

an orthorhombic prism with sides (a, a, c) or on a square, with the geometric center at the origin, as in Fig. 1. For molecular (site point) groups $g = T_d$, D_{2d}, and C_{4v} with $\sum_{n=1}^{4} \boldsymbol{r}_n = 0$, the relative spin positions are

$$\boldsymbol{r}_n = -\frac{a}{2}[\gamma_n^+ \hat{\boldsymbol{x}} + (-1)^n \hat{\boldsymbol{y}}] + \frac{c}{2}\gamma_n^- \hat{\boldsymbol{z}}, \qquad (1)$$

$$\gamma_n^\pm = \epsilon_n^+ (-1)^{n/2} \pm \epsilon_n^- (-1)^{(n+1)/2}, \qquad (2)$$

where $\epsilon_n^\pm = [1 \pm (-1)^n]/2$.[14] In tetrahedrons with $g = T_d$, $c/a = 1$, approximately as in Co_4 and Cr_4.[8, 9] In squares with $g = C_{4v}$, $c = 0$, as in one Mn_4 SMM and Nd_4 (with equal total angular momentum $j = 9/2$).[12, 15, 16] In prisms with $g = D_{2d}$, $c/a > 1$, approximately as in Ni_4, a Fe_4 and a Cu_4,[10] or $c/a < 1$. $\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}$ are the molecular (or global) axes of each tetramer SMM.

The local (or single-ion) azimuthal vectors satisfying all $g = C_{4v}$ symmetries are $\hat{\boldsymbol{x}}_n^g = (-\gamma_n^+ \hat{\boldsymbol{x}} + \gamma_n^- \hat{\boldsymbol{y}})/\sqrt{2}$, as in the right panel of Fig. 1, and the common local axial vector is $\hat{\boldsymbol{z}}_n^g = \hat{\boldsymbol{z}}$. For $g = T_d, D_{2d}$, we take the group symmetry-satisfying local axial vectors to be $\hat{\boldsymbol{z}}_n^g = \boldsymbol{r}_n/a_0$, as in the left panel of Fig. 1, where $a_0 = \sqrt{2a^2 + c^2}$, and we set $\overline{c} = c/a_0$ and $\overline{a} = a/a_0 = \sqrt{(1 - \overline{c}^2)/2}$. We define the local azimuthal vectors from $(\hat{\boldsymbol{z}}_1^g)^T = (\overline{a}, \overline{a}, \overline{c})$,

$$\hat{\boldsymbol{x}}_1^g = \frac{1}{2} \begin{pmatrix} -(1 + \overline{c})\cos\mu + (1 - \overline{c})\sin\mu \\ (1 - \overline{c})\cos\mu - (1 + \overline{c})\sin\mu \\ 2\overline{a}(\sin\mu + \cos\mu) \end{pmatrix}, \quad (3)$$

and $\hat{\boldsymbol{y}}_1^g = \hat{\boldsymbol{z}}_1^g \times \hat{\boldsymbol{x}}_1^g$. For $\mu = 0$, $\hat{\boldsymbol{x}}_1^g \cdot \hat{\boldsymbol{z}}_1^g = 0$. A rotation by the arbitrary angle μ about $\hat{\boldsymbol{z}}_1^g$ leads to Eq. (3). The

other local azimuthal vectors are obtained by π rotations of $\hat{\boldsymbol{x}}_1^g, \hat{\boldsymbol{y}}_1^g$ about $\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}$. They automatically satisfy all of the mirror planes of D_{2d}. [14] Although μ is a degree of freedom in D_{2d}, no μ choice satisfies the remaining group operations (rotations by $\pm 2\pi/3$ about the cube diagonals) of T_d. Hence, T_d only has local axial vectors.

In the local coordinates of groups $g = T_d$, D_{2d}, C_{4v}, the most general quadratic single-ion Hamiltonian is

$$\mathcal{H}_{si}^g = -\sum_n \Big(J_a(\boldsymbol{S}_n \cdot \hat{\boldsymbol{z}}_n^g)^2 \\ + J_e[(\boldsymbol{S}_n \cdot \hat{\boldsymbol{x}}_n^g)^2 - (\boldsymbol{S}_n \cdot \hat{\boldsymbol{y}}_n^g)^2] \Big), \quad (4)$$

which for these equal-spin, high symmetry systems has site-independent J_a, J_e. $\mathcal{H}_{si}^g$ is invariant under all allowed g symmetries. Unequal spin values or ligands or local structural distortions from the ideal molecular group symmetry, as commonly occur in real systems,[17] break these g symmetries, and also lead to Dzyaloshinshii-Moriya (DM) interactions, which vanish for precise molecular groups T_d, D_{2d}, or C_{4v}.[18, 19] Such lower symmetry cases will be discussed elsewhere.[20]

To make contact with experiment, we rewrite $\mathcal{H}_{si}^g$ in the molecular $(\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}})$ representation,

$$\tilde{\mathcal{H}}_{si}^g = -\sum_n \Big(J_z^g(\mu) S_{n,z}^2 + J_{xy}^g(\mu)(S_{n,x}^2 - S_{n,y}^2) \\ + \sum_{\alpha \neq \beta} J_{n,\alpha\beta}^g(\mu)\{S_{n,\alpha}, S_{n,\beta}\} \Big), \quad (5)$$

$$J_z^{D_{2d}}(\mu) = J_a(\overline{c}^2 - \overline{a}^2) + 3J_e\overline{a}^2 \sin(2\mu), \quad (6)$$
$$J_{xy}^{D_{2d}}(\mu) = J_e\overline{c}\cos(2\mu), \quad (7)$$

where $\alpha, \beta = x, y, z$, and the remaining non-vanishing couplings are $J_z^{C_{4v}} = J_a - J_e/2$, $J_{xy}^{C_{4v}} = J_e(-1)^n/2$, $J_{n,xy}^{D_{2d}}(\mu) = \gamma_n^-[J_a\overline{a}^2 + J_e(1 - \overline{a}^2)\sin(2\mu)]$, $J_{n,xz}^{D_{2d}}(\mu) = J_n^+(\mu)$, $J_{n,yz}^{D_{2d}} = -\gamma_n^- J_n^-(\mu)$, $J_n^\pm(\mu) = (-1)^n \overline{a}(J_a\overline{c} + J_e[\cos(2\mu) \pm \overline{c}\sin(2\mu)])$. In Eq. (5), $\{A, B\} = AB + BA$ and we subtracted an irrelevant constant. To preserve the g symmetries of $\mathcal{H}_{si}^g$, $\tilde{\mathcal{H}}_{si}^g$ contains the site-dependent interactions $J_{n,\alpha\beta}^g(\mu)$. The continuous (rotational) symmetry of the local azimuthal vectors in D_{2d} leads to anisotropy energy strengths in $\tilde{\mathcal{H}}_{si}^g$ that are periodic functions of μ, as in one-dimensional optical phonon bands.

We assume a molecular Hamiltonian of $\mathcal{H} = \mathcal{H}_0 + \tilde{\mathcal{H}}_{si}^g + \mathcal{H}_p$, where the Heisenberg and Zeeman interactions are

$$\mathcal{H}_0 = -J\boldsymbol{S}^2/2 - \gamma \boldsymbol{B} \cdot \boldsymbol{S} - \delta J^g(\boldsymbol{S}_{13}^2 + \boldsymbol{S}_{24}^2)/2, \quad (8)$$

where $\delta J^g = 0, J' - J$, and $-J$ for $g = T_d, D_{2d}$, and C_{4v} respectively, $\boldsymbol{S}_{13} = \boldsymbol{S}_1 + \boldsymbol{S}_3$, $\boldsymbol{S}_{24} = \boldsymbol{S}_2 + \boldsymbol{S}_4$, $\boldsymbol{S} = \boldsymbol{S}_{13} + \boldsymbol{S}_{24}$, $\gamma = g\mu_B$ is the gyromagnetic ratio (assumed isotropic, with $g \approx 2$), and $\boldsymbol{B} = B(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ is the magnetic induction at an arbitrary direction (θ, ϕ) relative to the molecular coordinates. The time correlation functions of the classical analog of this C_{4v} $\mathcal{H}_0$ model were published.[16]

The phenomenological global anisotropy interactions usually studied in SMM's are

$$\mathcal{H}_p = -J_b S_z^2 - J_d(S_x^2 - S_y^2), \quad (9)$$

containing axial and azimuthal contributions, respectively.[1] They are generally defined relative to the global spin principal axes, which for equal spin, high symmetry systems are the molecular axis vectors.

To take proper account of $\boldsymbol{B}$ in $\mathcal{H}_0$, we construct our SMM eigenstates in the induction representation by $(\hat{\tilde{\boldsymbol{x}}}, \hat{\tilde{\boldsymbol{y}}}, \hat{\tilde{\boldsymbol{z}}}) = (\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}) \cdot \overleftrightarrow{M}$ so that $\boldsymbol{B} = B\hat{\tilde{\boldsymbol{z}}}$,[4] where

$$\overleftrightarrow{M} = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{pmatrix}. \quad (10)$$

A subsequent arbitrary rotation about $\hat{\tilde{\boldsymbol{z}}}$ does not affect the eigenstates.[4] We then set $\hbar = 1$ and write

$$\boldsymbol{S}^2|\psi_{s,m}^{s_{13},s_{24}}\rangle = s(s+1)|\psi_{s,m}^{s_{13},s_{24}}\rangle, \quad (11)$$
$$\boldsymbol{S}_{13}^2|\psi_{s,m}^{s_{13},s_{24}}\rangle = s_{13}(s_{13}+1)|\psi_{s,m}^{s_{13},s_{24}}\rangle, \quad (12)$$
$$\boldsymbol{S}_{24}^2|\psi_{s,m}^{s_{13},s_{24}}\rangle = s_{24}(s_{24}+1)|\psi_{s,m}^{s_{13},s_{24}}\rangle, \quad (13)$$
$$S_{\tilde{z}}|\psi_{s,m}^{s_{13},s_{24}}\rangle = m|\psi_{s,m}^{s_{13},s_{24}}\rangle, \quad (14)$$
$$S_{\tilde{\sigma}}|\psi_{s,m}^{s_{13},s_{24}}\rangle = A_s^{\tilde{\sigma}m}|\psi_{s,m+\tilde{\sigma}}^{s_{13},s_{24}}\rangle, \quad (15)$$
$$A_s^m = \sqrt{(s-m)(s+m+1)}, \quad (16)$$

where $S_{\tilde{\sigma}} = S_{\tilde{x}} + i\tilde{\sigma}S_{\tilde{y}}$ with $\tilde{\sigma} = \pm$. For brevity, we denote $\nu = \{s, m, s_{13}, s_{24}, \{s_n\}\}$, and write $|\nu\rangle \equiv |\psi_{s,m}^{s_{13},s_{24}}\rangle$. From Eqs. (11) to (14), $\langle\nu'|\mathcal{H}_0|\nu\rangle = E_{\nu,0}\delta_{\nu',\nu}$, where

$$E_{\nu,0} = -Js(s+1)/2 - \gamma Bm \\ -\delta J^g[s_{13}(s_{13}+1) + s_{24}(s_{24}+1)]/2. \quad (17)$$

We then transform $\tilde{\mathcal{H}}_{si}^g$ and $\mathcal{H}_p$ to the induction representation, and make a standard perturbation expansion for small anisotropy energies $\{J_j\} = (J_a, J_b, J_d, J_e)$ relative to $|J|$ and γB.[4] The matrix elements of $\mathcal{H}_p$ are then obtained from Eqs. (14) and (15). However, the matrix elements of $\tilde{\mathcal{H}}_{si}^g$ contain more interesting physics.

By using symbolic manipulation software for the Clebsch-Gordan algebra, we find the single-ion spin matrix elements with general $\{s_n\} = (s_1, s_2, s_3, s_4)$ to be

$$\langle\nu'|S_{n,\tilde{z}}|\nu\rangle = \delta_{m',m}\Big(m\delta_{s',s}\Gamma_{s_{13},s'_{13},s_{24},s'_{24}}^{\{s_n\},s,i} \\ + \delta_{s',s+1}C_{-s-1}^m\Delta_{s_{13},s'_{13},s_{24},s'_{24}}^{\{s_n\},-s-1,n} \\ + \delta_{s',s-1}C_s^m\Delta_{s_{13},s'_{13},s_{24},s'_{24}}^{\{s_n\},s,n} \Big), \quad (18)$$

$$\langle\nu'|S_{n,\tilde{\sigma}}|\nu\rangle = \delta_{m',m+\tilde{\sigma}}\Big(A_s^{\tilde{\sigma}m}\delta_{s',s}\Gamma_{s_{13},s'_{13},s_{24},s'_{24}}^{\{s_n\},s,n} \\ - \delta_{s',s+1}D_{-s-1}^{\tilde{\sigma},m}\Delta_{s_{13},s'_{13},s_{24},s'_{24}}^{\{s_n\},-s-1,n} \\ + \delta_{s',s-1}D_s^{\tilde{\sigma},m}\Delta_{s_{13},s'_{13},s_{24},s'_{24}}^{\{s_n\},s,n} \Big), \quad (19)$$

$$C_s^m = \sqrt{s^2 - m^2}, \tag{20}$$

$$D_s^{\tilde{\sigma},m} = \tilde{\sigma}\sqrt{(s-\tilde{\sigma}m)(s-\tilde{\sigma}m-1)}, \tag{21}$$

$$\Gamma_{s_{13},s_{13}',s_{24},s_{24}'}^{\{s_n\},s,n} = \delta_{s_{24}',s_{24}}\epsilon_n^-\alpha_{s_1,s_3}^{s_{24},s,n}(s_{13},s_{13}')$$
$$+\delta_{s_{13}',s_{13}}\epsilon_n^+\alpha_{s_2,s_4}^{s_{13},s,n}(s_{24},s_{24}'), \tag{22}$$

$$\Delta_{s_{13},s_{13}',s_{24},s_{24}'}^{\{s_n\},s,n} = \delta_{s_{24}',s_{24}}\epsilon_n^-\beta_{s_1,s_3}^{s_{24},s,n}(s_{13},s_{13}')$$
$$+\delta_{s_{13}',s_{13}}\epsilon_n^+\beta_{s_2,s_4}^{s_{13},s,n}(s_{24},s_{24}'), \tag{23}$$

$$\alpha_{s_1,s_3}^{s_{24},s,n}(s_{13},s_{13}') = \frac{1}{4}(1+\xi_{s,s_{13},s_{24}})\delta_{s_{13}',s_{13}}$$
$$-\gamma_n^+\Big(F_{s_1,s_3,s}^{s_{13},s_{24}}\delta_{s_{13}',s_{13}-1}$$
$$+F_{s_1,s_3,s}^{s_{13}+1,s_{24}}\delta_{s_{13}',s_{13}+1}\Big), \tag{24}$$

$$\beta_{s_1,s_3}^{s_{24},s,n}(s_{13},s_{13}') = -\frac{(-1)^n}{4}\eta_{s,s_{13},s_{24}}\delta_{s_{13}',s_{13}}$$
$$-\gamma_n^+\Big(G_{s_1,s_3,s}^{s_{13},s_{24}}\delta_{s_{13}',s_{13}-1}$$
$$+G_{s_1,s_3,-s}^{s_{13}+1,s_{24}}\delta_{s_{13}',s_{13}+1}\Big), \tag{25}$$

$$F_{s_1,s_3,s}^{s_{13},s_{24}} = -\frac{\eta_{s_{13},s_1,s_3}A_{s+s_{13}}^{s_{24}}A_{s_{24}}^{s-s_{13}}}{4s(s+1)}, \tag{26}$$

$$G_{s_1,s_3,s}^{s_{13},s_{24}} = \frac{\eta_{s_{13},s_1,s_3}A_{s+s_{13}}^{s_{24}}A_{s+s_{13}-1}^{s_{24}}}{4s\sqrt{4s^2-1}}, \tag{27}$$

$$\eta_{z,x,y} = \frac{A_{x+z}^y A_y^{x-z}}{\sqrt{z^2(4z^2-1)}}, \tag{28}$$

$$\xi_{z,x,y} = \frac{x(x+1)-y(y+1)}{z(z+1)}, \tag{29}$$

where γ_n^+ is given by Eq. (2). The prefactors m, $A_s^{\tilde{\sigma}m}$, C_s^m, C_{-s-1}^m, $D_s^{\tilde{\sigma},m}$, and $D_{-s-1}^{\tilde{\sigma},m}$ are consequences of the Wigner-Eckart theorem for a vector operator.[14] The challenge was to obtain the coefficients $\Gamma_{s_{13},s_{13}',s_{24},s_{24}'}^{\{s_n\},s,n}$ and $\Delta_{s_{13},s_{13}',s_{24},s_{24}'}^{\{s_n\},s,n}$. Their hierarchical structure based upon the unequal-spin dimer suggests that analogous coefficients with $n > 4$ may be obtainable.[4]

At arbitrary (θ,ϕ), the first order corrections $E_{\nu,1}^\mu = \langle\nu|\mathcal{H}_p + \tilde{\mathcal{H}}_{si}^g|\nu\rangle$ to the eigenstate energies are

$$E_{\nu,1} = \frac{\tilde{J}_{b,z}^{g,\overline{\nu}}(\mu)}{2}[m^2-s(s+1)] - J_z^g(\mu)b_{\overline{\nu}}$$
$$-\frac{[3m^2-s(s+1)]}{2}\Big(\tilde{J}_{b,z}^{g,\overline{\nu}}(\mu)\cos^2\theta$$
$$+\tilde{J}_{d,xy}^{g,\overline{\nu}}(\mu)\sin^2\theta\cos(2\phi)\Big), \tag{30}$$

$$\tilde{J}_{b,z}^{g,\overline{\nu}}(\mu) = J_b + J_z^g(\mu)a_{\overline{\nu}}, \tag{31}$$

$$\tilde{J}_{d,xy}^{g,\overline{\nu}}(\mu) = J_d + J_{xy}^g(\mu)a_{\overline{\nu}}, \tag{32}$$

$$a_{\overline{\nu}} = \frac{1}{4}\Big(1+\xi_{s,s_{13},s_{24}}^2 - \eta_{s,s_{13},s_{24}}^2 - \eta_{s+1,s_{13},s_{24}}^2\Big)$$

$$+2\Big(\sum_{\sigma=\pm1}\Big[\Big(F_{s_1,s_1,s}^{s_{13}+(\sigma+1)/2,s_{24}}\Big)^2$$
$$-\sum_{\sigma'=\pm1}\Big(G_{s_1,s_1,\sigma\sigma's+\sigma(1+\sigma')/2}^{s_{13}+(1+\sigma)/2,s_{24}}\Big)^2\Big]$$
$$+(s_{13}\leftrightarrow s_{24})\Big), \tag{33}$$

$$b_{\overline{\nu}} = \frac{1}{8}\sum_{\sigma'=\pm1}(2s+1+\sigma')^2\Big(\eta_{s+(1+\sigma')/2,s_{13},s_{24}}^2$$
$$+8\sum_{\sigma=\pm1}\Big[\Big(G_{s_1,s_1,\sigma\sigma's+\sigma(1+\sigma')/2}^{s_{13}+(1+\sigma)/2,s_{24}}\Big)^2$$
$$+(s_{13}\leftrightarrow s_{24})\Big]\Big), \tag{34}$$

where the interactions are given by and following Eq. (7), and $\overline{\nu} = \{s,s_{13},s_{24},s_1\}$ excludes m. Second order corrections to the energies, including the symmetry-induced site-dependent interactions in Eq. (5), will be presented elsewhere.[20] For T_d, these are important, because their site-independent single-ion interactions vanish.

For T_d, D_{2d}, or C_{4v} symmetries, $E_{\nu,1}$ has a form entirely analogous to that of the dimer,[4] except for the periodic μ-dependence of the D_{2d} interactions, which broadens the discrete energy levels into bands, akin to one-dimensional optical phonon modes. This and the strongly different dependencies upon the quantum numbers $\overline{\nu}$ of the coefficients of the single-ion and global anisotropy interactions can be employed to provide a definitive measure of J, δJ^g, and $\{J_j\}$. This allows us to determine how well the phenomenological global anisotropy parameters simulate the microscopic systems. We therefore present the Hartree approximation in the induction representation of four measurable quantities.

The Hartree approximation is accurate at low $k_B T/|J|$ and $\gamma B/|J|$ not too small,[4] where k_B is Boltzmann's constant. In this approximation, $E_\nu = E_{\nu,0} + E_{\nu,1}$ is given by Eqs. (17) and (30), respectively. We define $\mathrm{Tr}_\nu^g \equiv \sum_\nu \int_{E_{\nu,\min}}^{E_{\nu,\max}} \mathcal{D}_\nu^g(\epsilon)d\epsilon$. For $g = D_{2d}$, we set $E_\nu = E_{\nu+} + E_{\nu-}\sin(2\mu+\chi_\nu)$, where $E_{\nu\pm} = (E_{\nu,\max}\pm E_{\nu,\min})/2$. Then $\mathcal{D}_\nu^g(\epsilon) = \frac{1}{2}[(\epsilon-E_{\nu,\min})(E_{\nu,\max}-\epsilon)]^{-1/2}$ is sharply peaked at $E_{\nu,\max}, E_{\nu,\min}$. For $g = T_d, C_{4v}$, $\mathcal{D}_\nu^g(\epsilon) = \delta(\epsilon-E_\nu)$ and $E_{\nu,\max} > E_\nu > E_{\nu,\min}$. The partition function in the Hartree approximation is then $Z_g^{(1)} = \mathrm{Tr}_\nu^g e^{-\beta\epsilon}$, where $\beta = 1/(k_B T)$, $|s_1-s_3| \le s_{13} \le s_1+s_3$, $|s_2-s_4| \le s_{24} \le s_2+s_4$, $|s_{13}-s_{24}| \le s \le s_{13}+s_{24}$, and $-s \le m \le s$. Then, the Hartree magnetization $M_g^{(1)}(\boldsymbol{B},T) = \gamma\mathrm{Tr}_\nu^g(me^{-\beta\epsilon})/Z_g^{(1)}$ and specific heat

$$\frac{C_{g,V}^{(1)}}{k_B\beta^2} = \frac{\mathrm{Tr}_\nu^g(\epsilon^2 e^{-\beta\epsilon})}{Z_g^{(1)}} - \Big(\frac{\mathrm{Tr}_\nu^g(\epsilon e^{-\beta\epsilon})}{Z_g^{(1)}}\Big)^2. \tag{35}$$

The Hartree EPR absorption $\Im\chi_{-\sigma,\sigma}^{g,(1)}(\boldsymbol{B},\omega)$ for clockwise ($\sigma = 1$) or counterclockwise ($\sigma = -1$) circularly

polarized oscillatory fields normal to $\boldsymbol{B}$ is

$$\Im\chi_{-\sigma,\sigma}^{g,(1)} = \frac{\gamma^2}{Z_g^{(1)}}\mathrm{Tr}_\nu^g\mathrm{Tr}_{\nu'}^g e^{-\beta\epsilon}\big|M_{\nu,\nu'}\big|^2$$
$$\times\big[\delta(\epsilon-\epsilon'+\omega)-\delta(\epsilon'-\epsilon+\omega)\big], \quad (36)$$

where $M_{\nu,\nu'} = A_s^{\sigma m}\delta_{m',m+\sigma}\delta_{s',s}\delta_{s'_{13},s_{13}}\delta_{s'_{24},s_{24}}$ and $\mathrm{Tr}_{\nu'}^g = \sum_{\nu'}\int_{E_{\nu',\min}}^{E_{\nu',\max}}\mathcal{D}_{\nu'}^g(\epsilon')d\epsilon'$. The resonant inductions for $g = T_d, C_{4v}$ are strong and centered at

$$\gamma B_{\mathrm{res}}^{(1)} = \pm\omega + \frac{(2m+\sigma)}{2}\Big((1-3\cos^2\theta)\tilde{J}_{b,z}^{g,\overline{\nu}}(0)$$
$$-3\sin^2\theta\cos(2\phi)\tilde{J}_{d,xy}^{g,\overline{\nu}}(\pi/4)\Big). \qquad (37)$$

For $g = D_{2d}$, the weak center of each $B_{\mathrm{res}}^{(1)}$, Eq. (37), is equally surrounded by two strong resonances split by $\gamma\Delta B_{\mathrm{res}}^{(1)} = 2|\sigma J_e(z_{\nu'}-z_\nu)|$, where $z_\nu = \sqrt{x_\nu^2+y_\nu^2}$, $y_\nu = \frac{1}{2}\overline{c}a_{\overline{\nu}}[3m^2-s(s+1)]\sin^2\theta\cos(2\phi)$, and $x_\nu = \frac{3}{2}\overline{a}^2\{2b_{\overline{\nu}}+a_{\overline{\nu}}[s(s+1)\sin^2\theta+m^2(3\cos^2\theta-1)]\}$. For $\theta = 0$, $\gamma\Delta B_{\mathrm{res}}^{(1)} = 6\overline{a}^2|(2m+\sigma)a_{\overline{\nu}}J_e|$, nicely fitting $s = 4$ ($a_{\overline{\nu}} = 1/7$) data on three Ni$_4$ compounds. For $c/a \approx 1.1$, $|J_e| \approx 0.07$K, 0.63K, and 0.91K.[11] More $B_{\mathrm{res}}(\theta,\phi)$ data are urged.

The Hartree INS cross-section $S_g^{(1)}(\boldsymbol{B},\boldsymbol{q},\omega)$ is

$$S_g^{(1)} = \mathrm{Tr}_\nu^g\sum_{\nu'}e^{-\beta\epsilon}\sum_{\tilde{\alpha},\tilde{\beta}}\big(\delta_{\tilde{\alpha},\tilde{\beta}}-\hat{q}_{\tilde{\alpha}}\hat{q}_{\tilde{\beta}}\big)\sum_{n,n'=1}^4$$
$$\times e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_n-\boldsymbol{r}_{n'})}\langle\nu|S_{n',\tilde{\alpha}}^\dagger|\nu'\rangle\langle\nu'|S_{n,\tilde{\beta}}|\nu\rangle, \quad (38)$$

where $\tilde{\alpha},\tilde{\beta} = \tilde{x},\tilde{y},\tilde{z}$, $\hat{q}_{\tilde{x}} = \sin\theta_{b,q}\cos\phi_{b,q}$, $\hat{q}_{\tilde{y}} = \sin\theta_{b,q}\sin\phi_{b,q}$, and $\hat{q}_{\tilde{z}} = \cos\theta_{b,q}$, $\theta_{b,q}$ and $\phi_{b,q}$ describe the relative orientations of $\boldsymbol{B}$ and $\boldsymbol{q}$,[4] the $\boldsymbol{r}_n$ and $\langle\nu'|S_{n,\tilde{\alpha}}|\nu\rangle$ are given by Eqs. (1), (18), and (19) respectively, and the scalar $\boldsymbol{q}\cdot(\boldsymbol{r}_n-\boldsymbol{r}_{n'})$ is invariant under the rotation, Eq. (10). As for the dimer,[4] additional EPR and INS transitions with amplitudes higher order in the $\{J_j\}$ are obtained in the extended Hartree approximation, but will be presented elsewhere for brevity.[20]

We presented a microscopic theory of high-symmetry single molecule magnets. From our exact single-ion spin matrix elements for four general spins, we studied the most general quadratic single-ion interactions in equal-spin tetramers with molecular group symmetry T_d, D_{2d}, or C_{4v}. Each group introduces site-dependent single-ion interactions, and azimuthal anisotropy with D_{2d} symmetry has a continuous symmetry observed as splittings in Ni$_4$ EPR resonances, providing a direct measure of the microscopic interaction. We used the Hartree approximation to provide explicit expressions for the magnetization, specific heat, EPR absorption, and INS cross-section, valid at low temperatures and sufficiently large magnetic fields. Our procedure is extendable to systems with lower symmetry, higher-order single-ion interactions, and possibly to systems with $n > 4$ spins.

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